

Assessment of NORM in bauxite residue to facilitate valorization

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Abstract

In the new Euratom Basic Safety Standard (BSS), materials with elevated concentrations of natural radionuclides can be considered as a potential source of radiological exposure. Such materials are often found in mining and metal extractive industries, where natural radionuclides are likely to end up and accumulate in the residue streams. Radiological assessment of the produced residues is a first and often sufficient step to demonstrate worker safety against radiological exposure.

Bauxite Residue (BR) is an example of a material which has an elevated natural radionuclide concentration. BR used in this work is coming from Greece and was assessed to be below the BSS reference levels and therefore does not pose a significant risk of elevated radiological exposure. The processing of BR might result in further radionuclide accumulation in secondary residues, which also should be characterized to demonstrate the radiological safety of workers.

In this work, the radiological properties of the residues produced after applying different extractive techniques for the recovery of iron, alumina and Rare Earth Elements (REE) were examined. All the analyzed samples were produced at the laboratory scale. The results suggest that for these residues, there is no significant radionuclide accumulation which would cause potentially elevated radiological exposure.

Introduction

Bauxite residue (BR, also referred to as “red mud” or “bauxite tailings”) is a by-product of the aluminium industry, produced on average at the rate of 1 - 1.5 ton per ton of alumina, with annual worldwide generation rate above 140 - 150 million tons¹. During the Bayer process, bauxite ore undergoes extraction to form sodium aluminate which is subsequently converted to alumina. BR includes all the material which is not extracted in the aforementioned process, and may exhibit enriched concentrations of iron, titanium, Rare Earth Elements (REE) as well as natural radionuclides (uranium, thorium and potassium) that are abundant in the earth crust.

BR can be potentially used as a secondary raw material for the recovery of primary metals (i.e. iron, aluminium, titanium) as well as REEs. Significant research efforts have been made to develop novel and environmentally-friendly methods for BR valorization²⁻⁷. This paper covers a specific environmental consideration related to BR: the radionuclide concentrations and assessment of potential for elevated radiological exposure.

According to the new Euratom Basic Safety Standard (BSS)⁸, legislation of the EU member states should integrate protection from natural radiation to the same extent as other radiation-related practices. However, an exemption level is provided to processes dealing with natural radionuclides concentrations in materials lower than 1 kBq/kg of ²³⁸U, ²³²Th and their decay products, 10 kBq/kg of ⁴⁰K. These materials are considered to be unlikely to cause elevated exposure to ionizing radiation and therefore are exempt from radiological regulatory control.

To classify materials that contain elevated concentration of natural radionuclides, the term “Naturally Occurring Radioactive Material” (NORM) is used. For the purposes of this paper, “NORM” is defined to include only those materials which are subject to BSS regulatory control.

In the current article, valorization methods of Greek BR produced by Aluminum of Greece (AoG) are discussed. In comparing these results with other studies, it is helpful to keep in mind that radionuclide content of BR is site-specific and will differ significantly in various BRs produced worldwide⁹. Likewise, pertinent radiological legislation may vary in different countries of the world; the conclusions demonstrated here are based on the Euratom BSS, which is applicable in Member States of the European Union.

Measurement methods

Measurements of natural radionuclides and their decay products were performed with gamma-ray spectroscopy. ²²⁶Ra (decay product of ²³⁸U, used as proxy¹⁰), ²²⁸Ra and ²²⁸Th (decay products of ²³²Th) were studied by their decay products (as presented in Table 1). Secular equilibrium was assumed between measured and presented nuclides (the probes were kept for a month after preparation to ensure secular equilibrium is achieved). The measurements have been performed with High Purity Germanium (HPGe) coaxial detector GEM- 35200 (EG&G Ortec®).

Sample preparation

Solid samples of residues were mixed with larger volume of epoxy resin and homogenized. After solidification, the samples had the same geometry and a similar matrix to the standard material. Possible differences in the sample internal structure and chemical composition were corrected using EFFTRAN computer model¹¹.

Residues produced in liquid form were dried and then prepared similarly to solid samples.

Results

BR from the same batch produced by AoG has been distributed between researchers working on BR valorization, the radionuclide content of which is presented in Table 1. After recovery of valuable metals, secondary residues have been analyzed for radionuclide content and compared with the initial BR. Further results are reported in the form of enrichment factors,

presented in equation 1 as a ratio between activity concentration of secondary residue over BR.

$$C_{radionuclide,i} = \frac{A_{residue,i}}{A_{BR,i}} \quad (1)$$

Table 1: Measurements of radionuclide concentration in bauxite residue. Isotopes in brackets were used to measure parent nuclides. Uncertainties are reported at 2σ .

Isotope series	Isotope	Concentration [Bq/kg]
^{238}U	^{238}U (^{234}Th)	152 ± 5
	^{226}Ra (^{214}Pb)	174 ± 1
^{232}Th	^{228}Ra (^{228}Ac)	435 ± 6
	^{228}Th (^{212}Pb)	425 ± 10
^{40}K	^{40}K	22 ± 3

Recovery of iron

Two methods to recover iron from BR have been used: reductive smelting^{3,4} and reductive roasting⁵. Measurement results for residues produced with reductive smelting are summarized in Table 2. Residues (called slags) from three experiments have been analyzed; where residue 1 was produced using minimal quantities of fluxing materials. This resulted in rather high radionuclide accumulation ratio (~ 2.3 times) and for ^{228}Th concentration reached 1013 ± 32 Bq/kg, making this specific residue a NORM. The process was then optimized (higher ratio of flux materials was applied) and in two following experiments obtained enrichment factor for every observed radionuclide did not exceed screening value set in the BSS and the mean radionuclide concentration increase was 60% in both experiments.

Table 2: Radionuclide enrichment in residues produced by reductive smelting.

Isotope	Enrichment factor		
	Slag. 1	Slag. 2	Slag. 3
^{226}Ra	2.3	1.7	1.6
^{228}Ra	2.2	1.6	1.6
^{228}Th	2.4	1.6	1.6
Mean	2.3	1.6	1.6

Reductive roasting was an alternative method selected for recovery of iron from BR. Results of a single experiment are presented in Table 3. Here, two steps of magnetic separation have been performed and recovered iron has been analyzed (Magnetic fraction I and II) as well as non-magnetic residue. In this process it was observed, that the iron produced after both separation steps contained a higher radionuclide content, compared to initial BR, while in the residue, the radionuclide content remained similar to BR. Overall, the increase of the radionuclide quantity in the system can potentially be explained by the addition of metallurgical coal. This is to be confirmed by further measurements.

Table 3: Results of a single experiment of reductive roasting. Two steps of magnetic separation have been performed and the residue is presented in the form of a non-magnetic fraction.

Isotope	Enrichment factor		
	Magnetic I	Magnetic II	Non-magnetic
²²⁶ Ra	1.4	1.4	1.1
²²⁸ Ra	1.5	1.4	1.1
²²⁸ Th	1.5	1.3	0.9
Mean	1.5	1.4	1.0

Recovery of aluminium

Two alumina recovery methods were applied. Results presented in Table 5 correspond to combined samples from multiple experiments (e.g. Sinters I is a mixture of 4 experiments and Residue 1.1 are mixed residues from the same experiments, where in every single experiment system parameters were modified). This was done to obtain reasonable sample mass to perform radiological characterization.

Table 4: Two batches of samples have been prepared. For batch 1 (produced prior to process optimization) results of sinters and residues are provided. For batch 2 only residues have been analyzed.

Isotope	Enrichment factor									
	Batch 1				Batch 2					
	Sinters I	Sinters II	Residue I	Residue II	Res. 2.1	Res. 2.2	Res. 2.3	Res. 2.4	Res. 2.5	Res. 2.6
²²⁶ Ra	0.9	0.8	1.1	1.3	1.3	1.3	1.3	1.3	1.2	1.3
²²⁸ Ra	0.9	0.8	1.1	1.2	1.2	1.2	1.2	1.2	1.2	1.2
²²⁸ Th	0.9	0.9	1.2	1.3	1.3	1.2	1.2	1.2	1.2	1.2
Mean	0.9	0.9	1.1	1.3	1.3	1.3	1.3	1.2	1.2	1.2

The first studied method consisted of two primary stages: at first, soluble sodium aluminate is produced by adding sodium carbonate to BR¹² and the resulting sinters had slightly diluted radionuclide content compared to BR, as presented in Table 4. Next, sodium hydroxide was used to recover alumina and a solid residue was obtained. Samples from batch 1 have been prepared during process optimization and batch 2 was prepared after the process was optimized. The produced optimized residues show that radionuclide content increased by 20 - 30% compared to BR. This was well below radionuclide enrichment by iron recovery, which is explained by lower alumina content in BR and lower extracted material quantity.

Ionic leaching was an alternative method selected to recovery of alumina⁷. This method allows to dissolve primary metals as well as REE and scandium. Radiological analysis of produced residue is presented in Table 5. Two sample batches were produced: batch 1 during process optimization and batch 2 once the process was optimized. It can be seen, that accumulation of radionuclides in the second batch was significantly higher, which was explained by increased metal recovery rate in the subsequent experiments were optimized. Another observation made is that ²²⁸Th enrichment in the residues was always lower than the accumulation rate of radium isotopes (²²⁶Ra and ²²⁸Ra). It is expected, that a portion of thorium was dissolved in the process and recovered with the pregnant leachate solution. Further measurements are required to confirm this hypothesis.

Table 5: Two batches of samples have been prepared. batch 1 (produced during process optimization) and batch 2 obtained after experiment conditions were optimized.

Isotope	Enrichment factor				
	Batch 1			Batch 2	
	Res 1.1	Res 1.2	Res 1.3	Res. 2.1	Res. 2.2
²²⁶ Ra	1.1	1.1	1.4	1.4	1.5
²²⁸ Ra	1.1	1.1	1.1	1.4	1.3
²²⁸ Th	0.7	1	0.8	1.1	1.2
Mean	1	1	1.1	1.3	1.3

Recovery of trace metals

BR neutralized by carbon dioxide was used to recover trace metals with various acids, the method is described elsewhere². Residues produced with three different acids are summarized in Table 6. Residue 1 was produced after leaching with nitric acid, for residues 2 and 3 sulfuric and hydrochloric acids were used. The residues produced show maximum of 30% of radionuclide enrichment for a specific nuclide and 20% mean radionuclide enrichment.

Table 6: 3 experiments to recover trace metals with nitric, sulfuric and hydrochloric acids.

Isotope	Enrichment factor		
	HNO ₃	H ₂ SO ₄	HCl
²²⁶ Ra	1.2	1.1	1.2
²²⁸ Ra	1.2	1.1	1.2
²²⁸ Th	1.1	1.0	1.3
Mean	1.2	1.1	1.2

Summary

The general trend that was observed is that radionuclide accumulation after recovery of valuable metals from BR is not significant to produce NORM residue.

The exception to this trend was one residue (slag 1) produced with reductive smelting, in which the radionuclide content exceeded the exemption level of 1 kBq/kg set in the Euratom BSS, meaning that this particular slag is classified as NORM and subject to regulatory control. If a process involving this reductive smelting residue were used in industry, further radiological assessment would be needed to demonstrate the safety of workers. However, since radionuclide content is close to the exemption limit, it is expected that the standard protective measures utilized at metallurgical plants (respirators, gloves, protective goggles) would be sufficient to demonstrate the safety of workers. After some optimization of process parameters (material flux ratios), the radionuclide accumulation was lower in reductive smelting residue 1, and it also fell below the BSS exemption level.

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